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54 Current collector bonded to a solid polymer membrane.

57 The invention is a method of forming an assembly of an ion permeable membrane, electrode, and current collector, comprising the steps of:

(a) forming a foundation layer of a porous electrically conductive material;

(b) at least partially coating a fluoropolymer binder on at least one surface of the conductive foundation layer;

(c) applying a particulate catalyst material over the fluoropolymer binder on the foundation layer;

(d) dispersing a polymeric material as a solution or dispersion over the catalyst material in a manner to obtain penetration of the polymeric material into the porous foundation layer to form a substantially continuous coating on the catalyst material and the at least partially coated foundation layer; and

(e) applying heat and/or pressure to enhance the flow of the polymeric material into the foundation layer and around the catalyst material to obtain adherence of the catalyst material to the foundation layer and to sinter the polymer material into a substantially non-porous layer around the catalyst material.

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CURRENT COLLECTOR BONDED TO A SOLID POLYMER MEMBRANE

The invention relates to an improved method of manufacturing a current collector/catalyst electrode/membrane assembly which has increased electrical conductivity in the area between the catalyst electrode and the current collector. Such assemblies are useful in a variety of applications including, for example, fuel cells, water electrolysis cells, chlor-alkali cells, and the like. The assembly produced according to the present invention is substantially structurally stable which allows the membrane portion to be substantially thinner than those presently available, thereby reducing the ionic resistance of the membrane.

It is highly desirable, given the harsh conditions of many of the applications for the membrane, that the membrane portion of the assembly have substantial structural integrity. Thinner membranes have been viewed as fragile and yet thinner membranes are desirable due to their reduced ionic resistance. This requires a balance between providing adequate structural support for the assembly and yet reducing the membrane's thickness to reduce the ionic resistance of the membrane without a sacrifice in the structural integrity.

References which have a bearing on this invention include U. S. Patent No. 4,272,353, which discloses a surface abrading technique for scratching a solid polymer electrolyte (SPE) base member in preparation for subsequent treatment. U. S. Patent No. 4,272,560 describes a membrane having a cathode made of multiple coatings with a backing fabric; a dissolved copolymer is used in the fabrication of this electrode. U. S. Patent No. 4,182,670 discloses a combined cathode and diaphragm utilizing a spray coating of a metal substrate with powdered metal; a polymer impregnated diaphragm is also described. An electrode body having impregnated powdered metal (typically noble metals) is described in U. S. Patent No. 3,276,911, and it also mentions a permeable ionic electrolytic material. U. S. Patent No. 4,364,813 discloses catalytic particles deposited on an ion exchange material with a SPE membrane; additionally, this patent has an ion exchange feature mentioning a sulfonic group. U. S. Patent No. 4,366,041 describes a cathode and diaphragm assembly with a sacrificial film made of wax.

The present invention particularly describes a structurally stable electrode assembly which has lower ionic resistance in the membrane portion and which has higher electrical conductivity in the catalyst electrode and current collector portions. Membrane thinness is achieved without sacrifice of structural integrity and yet resistance to ionic movement through the membrane is reduced.

While the foregoing refers in general terms to the present assembly, the structure thereof and the method of manufacture are exemplified in the detailed description of the preferred embodiments following.

The invention particularly resides in a method of forming an assembly of an ion permeable membrane, electrode, and current collector, comprising the steps of:

(a) forming a foundation layer of a porous, electrically conductive material;

(b) at least partially coating a fluoropolymer binder on at least one surface of the foundation layer;

(c) applying a particulate catalyst material over the fluoropolymer binder on the foundation layer;

(d) dispersing a polymeric material as a solution or dispersion over the catalyst material in a manner to obtain penetration of the polymeric material into the porous foundation layer to form a substantially continuous coating on the catalyst material and the at least partially coated foundation layer; and

(e) applying heat and/or pressure to the assembly to enhance the flow of the polymeric material into the foundation layer and around the catalyst material to obtain adherence of the catalyst material to the foundation layer and to sinter the polymer material into a substantially non-porous layer around the catalyst material.

The foundation layer is an electrically conductive, hydraulically permeable matrix which acts as a current collector to transmit electrical energy to or from the electrode. It may be composed of a variety of substances, including carbon cloth, carbon paper, carbon felt, metallic screens, metallic felt, and porous metallic sheets. Preferably, however, the foundation layer is a carbon paper, which is readily available, performs well, is easily handled, and is relatively inexpensive.

The paper most preferably used in this invention is also one having low electrical resistivity, possessing sufficient strength for fabrication, and having adequate surface properties, such as roughness, to provide good bonding between the fluoropolymer binder and the foundation layer. It is also preferable to provide good electrical contact between the carbon paper and the catalytically active particles of the electrode.

As a beginning step, the foundation layer is at least partially coated with a suitable polymer binder. This polymer binder can be a fluorocarbon polymer, such as polytetrafluoroethylene sold under the trademark of Teflon. Other suitable poly-

mers can include thermoplastic, non-ionic forms of sulfonic acid copolymers; thermoplastic, non-ionic forms of carboxylic acid copolymers; and the like.

Particularly preferred as the fluoropolymer binder are thermoplastic, non-ionic forms of perfluorinated polymers described in the following U. S. Patent Nos. 3,282,875; 3,909,378; 4,025,405; 4,065,366; 4,116,888; 4,123,336; 4,126,588; 4,151,052; 4,176,215; 4,178,218; 4,192,725; 4,209,635; 4,212,713; 4,251,333; 4,270,996; 4,329,435; 4,330,654; 4,337,137; 4,337,211; 4,340,680; 4,357,218; 4,358,412; 4,358,545; 4,417,969; 4,462,877; 4,470,889; 4,478,695; and published European Patent Application 0,027,009. Such polymers usually have equivalent weights of from 500 to 2000.

Particularly preferred for use as the fluoropolymer binder are copolymer of monomer I with monomer II (as defined below). Optionally, a third type of monomer may be copolymerized with I and II.

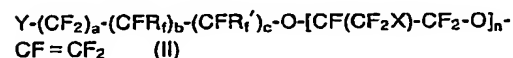
The first type of monomer is represented by general formula:



where:

Z and Z' are independently selected from -H, -Cl, -F, and -CF₃.

The second monomer consists of one or more monomers selected from compounds represented by the general formula:



where:

Y is selected from -SO₂Z, -CN, -COZ, and -C(R^{3f}f)(R^{4f}f)OH;

Z is selected from -I, -Br, -Cl, -F, -OR and -NR₁R₂; R is selected from a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

R^{3f}f and R^{4f}f are independently selected from perfluoroalkyl radicals having from 1 to 10 carbon atoms;

R₁ and R₂ are independently selected from -H, a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

a is 0-6;

b is 0-6;

c is 0 or 1;

provided a + b + c is not equal to 0;

X is selected from -Cl, -Br, -F, or mixtures thereof when n > 1;

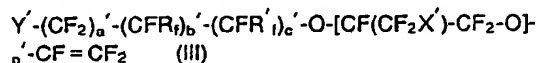
n is 0 to 6; and

R₁ and R₁' are independently selected from -F, -Cl,

perfluoroalkyl radicals having from 1 to 10 carbon atoms, and fluorochloroalkyl radicals having from 1 to 10 carbon atoms.

Particularly preferred is when Y is -SO₂F or -COOCH₃; n is 0 or 1; R₁ and R₁' are -F; X is -Cl or -F; and a + b + c is 2 or 3.

The third and optional monomer is one of more monomers selected from the compounds represented by the general formula:



where:

Y' is selected from -F, -Cl, or -Br;

a' and b' are independently 0-3;

c' is 0 or 1;

provided a' + b' + c' is not equal to 0;

n' is 0-6;

R₁ and R₁' are independently selected from -Br, -Cl, -F, perfluoroalkyl radicals having from 1 to 10 carbon atoms, and chloroperfluoroalkyl radicals having from 1 to 10 carbon atoms; and

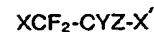
X' is selected from -F, -Cl, -Br, or mixtures thereof when n' > 1.

The binder is typically applied in a solution or dispersion to at least partially coat the foundation layer. The solution nor dispersion can be applied to the foundation layer using a variety of methods well known in the art.

When the electrode is to be used in a fuel cell, preferably, the binder is a hydrophobic material like polytetrafluoroethylene. When, however, the electrode is to be used in an electrolytic cell, such as a chlor-alkali cell, the binder is preferably a hydrophilic material like the copolymers formed from monomers I, II and, optionally III (described above).

The preferred loading, i.e. amount of application of the binder, is from 0.50 to 50 mg/cm² of foundation area with a preferred range of from 2.5 to 30 mg/cm² of foundation area.

When the binder is applied as a solution or a dispersion, the solvent/dispersant can be a variety of materials including, for example, water, methanol, ethanol, and compounds represented by the general formula:



wherein:

X is selected from F, Cl, Br, and I;

X' is selected from Cl, Br, and I;

Y and Z are independently selected from H, F, Cl, Br, I and R'; and

R' is selected from perfluoroalkyl radicals and chloroperfluoroalkyl radicals having from 1 to 6 carbon atoms.

The most preferred solvents or dispersants are

1,2-dibromotetrafluoroethane (commonly known as Freon 114 B 2)

$\text{BrCF}_2\text{-CF}_2\text{Br}$

and 1,2,3-trichlorotrifluoroethane (commonly known as Freon 113):

$\text{ClF}_2\text{C-CCl}_2\text{F}$

Of these two materials, 1,2-dibromotetrafluoroethane is the most preferred solvent or dispersant.

The solution or dispersion used to apply the binder to the foundation layer may have a concentration of from 2 to 30 weight percent of polymer in the solvent/dispersant. Preferably, the concentration is from 8 to 20 weight percent of polymer in the solvent/dispersant.

After the solution or dispersion has been applied to the foundation layer, the solvent can then be driven off using heat, a vacuum, or a combination of heat and a vacuum. Optionally, the solvent/dispersant may be allowed to evaporate under ambient conditions. Preferably, the solvent is removed at an elevated temperature. In addition to removing the solvent/dispersant, the heat sinters the binder and causes it to more completely penetrate and surround the foundation layer. As an example, when polytetrafluoroethylene is used as the binder, exposure at a temperature of from 300°C to 340°C for about 20 minutes will suffice to remove the solvent/dispersant and to sinter the polytetrafluoroethylene.

The next step in the method of the present invention is the application of catalytically active and electrically conductive particles to the coated foundation layer. The composite structure will, ultimately, form what is commonly referred to as a solid polymer electrolyte, or SPE, when the composite is used in an electrochemical cell. The electrode can be ultimately used as either a cathode or as an anode.

Materials suitable for use as electro-catalytically active anode materials include, for example, metals or metal oxides of platinum group metals, such as ruthenium, iridium, rhodium, platinum, palladium, either alone or in combination with an oxide of a film-forming metal such as Ti or Ta. Other suitable activating oxides include cobalt oxide, either alone or in combination with other metal oxides, such as those described in U. S. Patent Nos. 3,632,498; 4,142,005; 4,061,549; and 4,214,971.

Materials suitable for use as electro-catalytically active cathode materials include, for example, platinum group metals or metal oxides, such as ruthenium or ruthenium oxide. U. S. Patent No. 4,465,580 describes such cathodes.

The catalytic particles used in the present in-

vention are preferably finely divided and have a preferred range of from 270 to smaller than 400 mesh size (U. S. Standard) (53 to less than 37 microns). The metal powder is applied to the binder-coated foundation layer by methods known to those skilled in the art including, for example, spraying, forming a sheet of catalytic particles and pressing the sheet onto the foundation layer, or forming and applying the particles in the form of liquid dispersion, for example, an aqueous dispersion. A suitable loading of catalyst particles has been found to be from 0.2 to 20 mg/cm² of foundation area with a preferred range of from 1.5 to 5.0 mg/cm² of foundation area.

Separately, a copolymer is formed. One such suitable polymer is the polymer formed from monomers I, II, and optionally III, as defined above. The polymer may be a thermoplastic, non-ionic precursor of a sulfonic acid copolymer or a thermoplastic, non-ionic precursor of a carboxylic acid copolymer, or a variety of other polymers as defined for use as the binder. Preferably, the copolymer is formed into a solution or a dispersion with a solvent for application to the catalytically active particles. On mixing with a suitable solvent or dispersant, the polymer is applied to the catalyst particle coated foundation layer. Utilizing a vacuum on one side of the foundation layer, the polymer in the solvent or dispersant is pulled onto the catalyst and into the foundation layer. While in one sense it can be described as coated on one side, the coating nevertheless sufficiently penetrates into the porous sheet.

In the step of bonding a fluoropolymer onto the surface of the catalytic particle coated foundation layer, the most convenient procedure is the use of conventional organic solvents. Typical solvents used are 1,2-dibromotetrafluoroethane, methanol, ethanol, and the like. The polymeric material which is applied forms a substantially non-porous ion exchange layer.

The next step is the application of heat and/or pressure to remove the solvent/dispersant and to sinter the polymer, thereby forming the polymer into a substantially continuous sheet. In addition, the heat and/or pressure enhance the coating of the polymer around the catalyst particles and the foundation layer. For example, exposure to a temperature in the range of from 260°C to 320°C is generally suitable to bond the polymer to the particles and the foundation layer. The temperature range is limited primarily by the onset of thermal degradation of the polymer caused by excessive heat. The pressure is preferably sufficiently high and sustained for an interval to achieve bonding. In one example, pressure may be applied up to about 5 kg/cm² for about one minute at elevated temperature.

The next step in the manufacture of the improved electrode structure is to hydrolyze the structure from the non-ionic to the ionic form. Hydrolysis may be accomplished by treating the polymer with a basic solution if the polymer is a thermoplastic, non-ionic precursor of a sulfonic acid polymer or a thermoplastic, non-ionic precursor of a carboxylic acid polymer. In addition, if the polymer is a thermoplastic non-ionic precursor of a carboxylic acid polymer, an acid solution may be used to hydrolyze the polymer. For example, in a thermoplastic, non-ionic precursor of a sulfonic acid polymer, the completed structure may be hydrolyzed in 25 weight percent sodium hydroxide for 16 hours at an elevated temperature of 80° C.

The completed article is then ready for use. As an example of typical size, it is not uncommon to encounter a membrane which is in a range of from 5 to 10 mils (0.125 to 0.25 mm) thick due to the need for structural integrity. The finished product can yield a membrane with a thickness in a range of from 1 to 2 mils (0.025 to 0.05), or even less. The resistance of ionic movement through the membrane is thus lowered by a significant amount.

In an alternate application, two similar sheets of equal size are positioned in contact with one another in a manner so that the foundation layers face toward the outside of the combination and the polymer layer on each sheet is contacted against the polymer layer on the other sheet. The coterminous sheets are then placed into a press and on the application of suitable pressure/or heat, they are joined together.

Claims

1. A method of forming an assembly of an ion permeable membrane, electrode, and current collectors, comprising the steps of:

(a) forming a foundation layer of a porous, electrically conductive material;

(b) at least partially coating a fluoropolymer binder on at least one surface of the foundation layer;

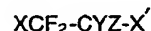
(c) applying a particulate catalyst material over the fluoropolymer binder on the foundation layer;

(d) dispersing a polymeric material as a solution or dispersion over the catalyst material in a manner to obtain penetration of the polymeric material into the porous foundation layer to form a substantially continuous coating on the catalyst material and the at least partially coated foundation layer; and

(e) applying heat and/or pressure to the assembly to enhance the flow of the polymeric material into the foundation layer and around the cata-

lyst material to obtain adherence of the catalyst material to the foundation layer and to sinter the polymeric material into a substantially non-porous layer around the catalyst material.

2. The method of Claim 1, wherein the polymeric material contains one or more solvents or dispersants selected from ethanol, methanol, water, and a compound represented by the general formula:



wherein:

X is selected from F, Cl, Br, and I;

X' is selected from Cl, Br, and I;

Y and Z are independently selected from H, F, Cl, Br, I, and R';

R' is selected from perfluoroalkyl radicals and chloroperfluoroalkyl radicals having from 1 to 6 carbon atoms.

3. The method of Claim 2, wherein the solvent or dispersant is selected from 1,2-dibromotetrafluoroethane and 1,2,3-trichlorotrifluoroethane.

4. The method of Claim 1, 2, or 3, wherein the catalyst particles are selected from ruthenium, iridium, rhodium, platinum, palladium, or oxides thereof either alone or in combination with an oxide of a film-forming metal, and cobalt oxide either alone or in combination with other platinum group metal or metal oxide.

5. The method of any one of the preceding claims including the step of making two similar sized assemblies, placing the two assemblies together such that the non-porous polymeric surfaces are in intimate contact with each other, and applying heat and/or pressure to form a single planar assembly containing two current collectors and having a non-porous, ionically conductive polymer layer therebetween.

6. The method of any one of the preceding claims, wherein said fluoropolymer binder for the foundation layer is a thermoplastic, non-ionic precursor of a sulfonic acid copolymer having an equivalent weight range of from 500 to 2000.

7. The method of any one Claims 1 to 5, wherein said fluoropolymer binder for the foundation layer is a thermoplastic, non-ionic precursor of a carboxylic acid copolymer.

8. The method of Claim 1, wherein:

(a) said conductive material is porous conductive graphite paper,

(b) said binder is polytetrafluoroethylene, and

(c) said polymeric material is a sulfonic acid copolymer in thermoplastic powder form in a liquid solvent and a vacuum is drawn to obtain penetration into the porous graphite paper.

9. The method of Claim 1, including the step of exposing the polymer to a base or to an acid at a temperature and for a time sufficient to hydrolyze substantially all of the polymer.

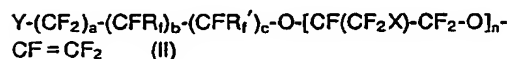
10. The method of any one of the preceding claims, wherein the binder is a copolymer formed from the polymerization of one or more monomers selected from the group of monomers represented by the general formula:



where:

Z and Z' are independently selected from -H, -Cl, -F, or -CF₃.

with one or more monomers selected from a second group of monomers represented by the general formula:



where:

Y is selected from -SO₂Z, -CN, -COZ, and -C(R^{3f})(R^{4f})OH;

Z is selected from -I, -Br, -Cl, -F, -OR and -NR₁R₂;
R is selected from a branched or linear alkyl radical having from 1 to 10 carbon atoms or an aryl radical;

R^{3f} and R^{4f} are independently selected from perfluoroalkyl radicals having from 1 to 10 carbon atoms;

R₁ and R₂ are independently selected from -H, a branched or linear alkyl radical having from 1 to 10 carbon atoms, and an aryl radical;

a is 0-6;

b is 0-6;

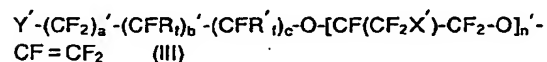
c is 0 or 1;

provided a + b + c is not equal to 0;

X is selected from -Cl, -Br, -F, and mixtures thereof when n > 1;

n is 0 to 6; and

R₁ and R₁' are independently selected from -F, -Cl, perfluoroalkyl radicals having from 1 to 10 carbon atoms, and fluorochloroalkyl radicals having from 1 to 10 carbon atoms, and optionally, one or more monomers selected from a third monomer represented by the general formula:



where:

Y' is selected from -F, -Cl, or -Br;

a' and b' are independently 0-3;

c' is 0 or 1;

provided a' + b' + c' is not equal to 0;

n' is 0-6;

R₁ and R₁' are independently selected from -Br, -Cl, -F, perfluoroalkyl radicals having from 1 to 10 carbon atoms, and chloroperfluoroalkyl radicals having from 1 to 10 carbon atoms; and

X' is selected from -F, -Cl, -Br, and mixtures thereof when n' > 1.

11. The method of Claim 10, wherein Y is -SO₂F or -COOCH₃; n is 0 or 1; R₁ and R₁' are -F; X is -Cl or -F; and a + b + c is 2 or 3.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 87 11 2758

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	GB-A-2 101 160 (DIAMOND SHAMROCK CORP.)		C 25 B 11/20 H 01 M 8/10
A	EP-A-0 228 602 (THE DOW CHEMICAL CO.)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 25 B 9 H 01 M 8 C 25 B 11
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-04-1988	Examiner GROSEILLER PH.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			